

Quantum thermodynamics in chiral two-level systems.

The quantum stochastic resonance

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Abstract

A Langevin canonical framework for a chiral two-level system coupled to a bath of harmonic oscillators is used within a coupling scheme different from the well-known spin-boson model. From this stochastic dynamics, within the Markovian regime and Ohmic friction, some standard quantum thermodynamics functions such as the energy average and heat capacity can be extracted. In particular, special emphasis is put on the so-called quantum stochastic resonance which is a cooperative effect of friction, noise and periodic driving occurring in a bistable system.

I. INTRODUCTION

Open quantum systems are nowadays a very active field of research due to the fact that the interaction with the environment can hardly be ignored in many physical, chemical and biological processes [1–3]. One of the most standard ways of analyzing the corresponding dynamics is by considering the system of interest and the environment as forming a whole closed system (the Universe). The so-called Caldeira-Leggett Hamiltonian is a very illustrative and convenient starting point for an open dynamics [4]. When tracing out the degrees of freedom of the environment in that dynamics, the resulting equations of motion for the system (in the Heisenberg picture of quantum mechanics) lead to some sort of coupled equations, being one of them a generalized Langevin equation. The presence of fluctuations of the environment makes that the system dynamical variables become stochastic processes. The generalized Langevin equation is transformed into a standard one when Ohmic (constant) friction is assumed.

An alternative approach can also be analyzed in terms of nonlinear quantum equations. One of them is the well known nonlinear, logarithmic Schrödinger equation proposed for an open dynamics due to Kostin [5]; in particular, for the Brownian motion (linear dissipation). This equation is known as the Schrödinger-Langevin or Kostin equation. Recently, an application of this equation to the harmonic oscillator under the presence of thermal fluctuations (white and colored) has been reported [6]. Furthermore, a generalized equation for nonlinear dissipation has also been proposed [7, 8].

On the other hand, the description of many phenomena in terms of a two level system (TLS) can also be found in the same fields of research mentioned before [9], going from chiral molecules, electron transfer reactions, high energy physics, quantum optics and computation to biological homochirality. Concerning molecular chirality, the pioneering work of Harris and Stodolsky [10] considered the effect of parity violation on the tunneling dynamics of chiral molecules, relating it to their optical activity (see also [11]). Based on this approach, the so-called parity violating energy difference (PVED) is considered to be one of the possible origins of molecular homochirality, which refers to the almost exclusive one-handedness of chiral molecules found in living systems (D-sugars and L-aminoacids). This is one of the fundamental problems of science which still remains unsolved [12]. Thus, chiral molecules could be used as a test for parity violating interactions since non conclusive results for

electroweak parity violation would allow us to put some stringent bounds on parity-violating interactions different from the electroweak one. In particular, in light of the recent advances on molecular PVEDs, some spin-dependent gravitational theories can be devised and studied [13, 14].

In a series of papers [15–18], the authors have studied a chiral TLS in presence of an environment (harmonic bath) leading to a more realistic analysis of chiral dynamics. The TLS is modelled by a two-well (asymmetric) potential within the Born-Oppenheimer approximation. A canonical formalism has been proposed where the populations and coherences, through the phase difference, are seen as stochastic processes, both of them being related to their optical properties. The time evolution of the nonisolated chiral TLS has provided information about the coherent and incoherent tunneling. This theoretical analysis has also allowed us to successfully study some thermodynamical properties of these systems from a stochastic dynamics. In general, there are several routes to reach thermodynamical properties such as partition functions, thermal averages, heat capacity, entropy, etc. Very likely, the most popular one is that based on the thermodynamic method coming from the path-integral formalism. An extensive account of this formalism can be found in Weiss’s book [1]. However, numerical instability problems from the analytic continuation of certain functions lead to some drawbacks. As an alternative way to avoid such problems, the computation of thermodynamics from a stochastic dynamics is carried out here presenting some advantages. Thus, partition functions and canonical thermal averages are then calculated when carrying out dynamical calculations for different bias or asymmetry. Analogously, one can also obtain the main equilibrium thermodynamics properties of the non-isolated TLS from the stochastic dynamics at asymptotic times (if the dynamics is ergodic) for a given bias and different temperatures. Furthermore, it is worth stressing that the thermodynamic functions are independent on the friction coefficient in the weak coupling limit. Therefore, our thermodynamical average values coming of solving the corresponding stochastic dynamics are independent on the friction coefficient as time goes to infinity, that is, when the thermal equilibrium with the bath is reached. In the strong coupling limit, this fact no longer holds [19]. A dynamical viewpoint has also been proposed within the density matrix formalism [20].

As a new extension of this work, the so-called quantum stochastic resonance (QSR) [21] provides a natural scenario to apply our canonical formalism. Very briefly, this process refers

to the amplification of the response to an external periodic signal at a certain value of the noise strength, being a cooperative effect of friction, noise and periodic driving occurring in a bistable system. Classically, the output signal is maximum when the thermal hopping rate is in resonance with the frequency of the driving force. However, the quantum counterpart of this process seems to reveal new features. Time-dependent bias effects have been used to enhance the very elusive parity violation effects in molecules previously commented. In particular, a proposal to detect parity violation effects in diatomic molecules by DeMille *et al.* [22] is currently ongoing and seems to be very promising (see [23] and references therein). In addition, a very recent work by Harris and Walls [24] proposes to use an AC electric field that is resonantly modulated at the Larmor frequency to enhance the chiral term effects which appear when an electric field is coupled to nuclear magnetic resonance effects in chiral molecules [25]. In this spirit, QSR would constitute a good playground where parity violating effects in chiral molecules could be tested. In a previous work [26], within the linear response regime, we have shown that an external driving field that lowers and rises alternatively each one of the minima of the well, a signal of QSR should be observed only in the case that the PVED is different from zero, the resonance condition being independent on tunneling between the two enantiomers.

In this work, we are going to briefly review the analysis of the quantum thermodynamics issued from a chiral TLS. Afterwards, we focus mainly on the observation of QSR in chiral molecules within the canonical formalism previously developed. From this simple analysis, some important consequences on the possible detection of the PVED between chiral molecules are directly deduced.

II. A DYNAMICAL THEORY OF QUANTUM THERMODYNAMICS

A. A canonical formalism for an isolated (closed) chiral two level system

Let us describe an isolated TLS by the Hamiltonian $\hat{H} = \delta\hat{\sigma}_x + \epsilon\hat{\sigma}_z$, where $\sigma_{x,z}$ stand for the Pauli matrices. The isolated TLS is usually considered as a good model for a two-well (asymmetric) potential within the Born-Oppenheimer approximation. From the knowledge of the eigenstates, $|1\rangle, |2\rangle$, the left and right states (or chiral states), $|L\rangle$ and $|R\rangle$, respectively, can be expressed by means of a rotation angle θ given by $\tan 2\theta = \delta/\epsilon$, where $\langle L|\hat{H}|R\rangle = -\delta$

(with $\delta > 0$) accounts for the tunneling rate and $2\epsilon = \langle L|\hat{H}|L\rangle - \langle R|\hat{H}|R\rangle$ (ϵ can be positive or negative) for the asymmetry due to the electroweak parity violation [10, 11] (for a chiral system) or any other bias term.

Among other interesting and more geometric representations of the isolated TLS [27, 28], an alternative and useful way of looking at it is based on the polar form of the complex amplitudes defining the wave function $|\Psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle$, solution of the time-dependent Schrödinger equation ($\hbar = 1$). If the complex amplitudes are expressed as $a_{L,R}(t) = |a_{L,R}(t)|e^{i\Phi_{L,R}(t)}$, and the population and phase differences between chiral states are defined as $z(t) \equiv |a_R(t)|^2 - |a_L(t)|^2$ and $\Phi(t) \equiv \Phi_R(t) - \Phi_L(t)$, respectively, it can be shown that the average energy in the normalized $|\Psi(t)\rangle$ state is given by $\langle\Psi|\hat{H}|\Psi\rangle = -2\delta\sqrt{1-z^2}\cos\Phi + 2\epsilon z \equiv H_0$, where H_0 represents a Hamiltonian function. Since z and Φ can be seen as a pair of canonically conjugate variables, the Heisenberg equations of motion (which are formally identical to the Hamilton equations) are easily derived from $\dot{z} = -\partial H_0/\partial\Phi$ and $\dot{\Phi} = \partial H_0/\partial z$. Explicitly, the non-linear coupled equations describing an isolated TLS in these canonical variables are [15–18]

$$\begin{aligned}\dot{z} &= -2\delta\sqrt{1-z^2}\sin\Phi \\ \dot{\Phi} &= 2\delta\frac{z}{\sqrt{1-z^2}}\cos\Phi + 2\epsilon.\end{aligned}\tag{1}$$

Thus, Eqs. (1) are totally equivalent to the usual time-dependent Schrödinger equation. For simplicity, the adimensional time $t \rightarrow 2\delta t$ will be used in the rest of this work. This re-scaling implies that the Hamiltonian function H_0 can again be expressed as

$$H_0 = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z.\tag{2}$$

It should be emphasized that the first term of the Hamiltonian function (2) accounts for the tunneling process and, the second one, for the underlying asymmetry (due to a bias or the PVED between enantiomers), showing clearly the two competing processes in this dynamics. In particular, the ratio ϵ/δ gives us an indication of the importance of each contribution.

The connection to the density matrix formalism is readily obtained from the corresponding matrix elements expressed as $\rho_{R,R} = |a_R|^2$, $\rho_{L,L} = |a_L|^2$, $\rho_{L,R} = a_L a_R^*$ and $\rho_{R,L} = a_R a_L^*$.

Thus, the time average values of the Pauli operators are given by

$$\begin{aligned}\langle \hat{\sigma}_z \rangle_t &= \rho_{R,R} - \rho_{L,L} = z \\ \langle \hat{\sigma}_x \rangle_t &= \rho_{R,L} + \rho_{L,R} = -\sqrt{1-z^2} \cos \Phi \\ \langle \hat{\sigma}_y \rangle_t &= i\rho_{R,L} - i\rho_{L,R} = \sqrt{1-z^2} \sin \Phi,\end{aligned}\tag{3}$$

which is consistent with $\langle \hat{H} \rangle = \delta \langle \hat{\sigma}_x \rangle + \epsilon \langle \hat{\sigma}_z \rangle$ and

$$\langle \hat{\sigma}_x \rangle_t^2 + \langle \hat{\sigma}_y \rangle_t^2 + \langle \hat{\sigma}_z \rangle_t^2 = 1.\tag{4}$$

The time population difference can also be split into two components which are symmetric and antisymmetric under the inversion operation consisting of replacing ϵ by $-\epsilon$.

B. Stochastic dynamics for an open chiral two level system

When dealing with interactions with the environment consisting of a high number of degrees of freedom, more sophisticated theoretical approaches are needed. Among the different formalisms incorporating the interaction with the environment [1, 2], the canonical formalism issued from a Caldeira–Leggett–like Hamiltonian [9] is very often used. A bilinear coupling between the TLS and an environment is in general assumed. In particular, for the Hamiltonian function of the isolated TLS given by Equation (2), we have recently developed this formalism to study the dissipative dynamics of chiral systems [15–18]. Within the Markovian regime, the corresponding dynamics is given by the following coupled differential equations

$$\begin{aligned}\dot{z} &= -\sqrt{1-z^2} \sin \Phi - \gamma \dot{\Phi}(t) + \xi(t) \\ \dot{\Phi} &= \frac{z}{\sqrt{1-z^2}} \cos \Phi + \frac{\epsilon}{\delta}.\end{aligned}\tag{5}$$

In this regime, the standard properties of the fluctuation force $\xi(t)$, assumed to be a Gaussian white noise, are given by the following canonical thermal averages or properties: $\langle \xi(t) \rangle_\beta = 0$ (zero average) and $\langle \xi(0)\xi(t) \rangle_\beta = mk_B T \gamma \delta(t)$ (delta-correlated) where $\beta = (k_B T)^{-1}$, k_B being Boltzmann’s constant. The friction is then described by $\gamma(t) = 2\gamma \delta(t)$, where γ is a constant and $\delta(t)$ is Dirac’s δ -function (not to be confused with the δ -parameter describing the tunneling rate). The following condition is always satisfied [1, 28]

$$\langle \hat{\sigma}_x \rangle_t^2 + \langle \hat{\sigma}_y \rangle_t^2 + \langle \hat{\sigma}_z \rangle_t^2 < 1.\tag{6}$$

The corresponding solutions provide stochastic trajectories for the population, z , and phase differences, Φ , encoding all the information on the dynamics of the non-isolated TLS. These solutions are dependent on the four dimensional parameter space $(\epsilon, \delta, \gamma, T)$, apart from the initial conditions $z(0) = z_0$ and $\Phi(0) = \Phi_0$. Interestingly enough, an effective Hamiltonian function which explicitly depends on the friction and noise can be extracted from the Hamilton equations given by Eq. (5),

$$H_{\gamma, \xi}(z, \Phi) = -\sqrt{1-z^2} \cos \Phi + \frac{\epsilon}{\delta} z + \gamma \Phi \left(\frac{z}{\sqrt{1-z^2}} \cos \Phi + \frac{\epsilon}{\delta} \right) - \xi \Phi \quad (7)$$

which represents the non-conserved energy of the chiral system under the presence of the thermal bath and its mutual coupling as a function of time. This Hamiltonian function has also been extracted from a Caldeira-Leggett model as reported in Ref. [16]. This effective energy turns out to be critical for the evaluation of any thermodynamical function such as, for example, the heat capacity. In a certain sense, this information is the alternative way to the more standard one of using the partition function and density matrix for the reduced system [1, 20]. It gives us a simple procedure to evaluate time dependent energy fluctuations. The use of classical white noise imposes some restrictions on the range of temperatures where this approach remains valid. At high temperatures, $\beta^{-1} \gg \hbar\gamma$ (or $\gamma^{-1} \gg \hbar\beta$) thermal effects are going to be predominant over quantum effects which become relevant, in general, at times of the order of or less than $\hbar\beta$, sometimes also called thermal time. However, in general, at very low temperatures, $\beta^{-1} \ll \hbar\gamma$ (or $\gamma^{-1} \ll \hbar\beta$) the noise is colored and its correlation function is complex and our approach is no longer valid. The dissipative dynamics in the classical noise regime is obtained at zero noise or zero temperature [3].

A previous analysis of the thermodynamics of non-interacting chiral molecules assuming a canonical distribution has been carried out elsewhere [29]. In particular, thermal averages of pseudoscalar operators were extensively analyzed. The canonical thermal average of an observable X is defined as $\langle X \rangle_\beta = \text{Tr}(\rho_\beta X)$ where $\rho_\beta = Z^{-1} e^{-\beta \hat{H}}$. The quantum partition function Z is given by $Z = 2 \cosh(\beta \Delta)$ from the eigenvalues of H with $\Delta = \sqrt{\delta^2 + \epsilon^2}$ and the corresponding averages for the population difference and coherences (in the L-R basis) are then calculated to give

$$\begin{aligned} \langle z \rangle_\beta &\equiv \langle \hat{\sigma}_z \rangle_\beta = \frac{\epsilon}{\Delta} \tanh(\beta \Delta) \\ \langle \hat{\sigma}_x \rangle_\beta &= \frac{\delta}{\Delta} \tanh(\beta \Delta). \end{aligned} \quad (8)$$

From the knowledge of the partition function, the remaining equilibrium thermodynamical functions are easily deduced such as the Helmholtz free energy, the entropy, the heat capacity, etc. [29]. For example, the thermal average of the energy has been showed to be

$$\langle E \rangle_\beta = E_0 - \Delta \tanh(\beta\Delta). \quad (9)$$

Usually, the origin of the energy is taken to be $E_0 = (\langle L|\hat{H}|L\rangle + \langle R|\hat{H}|R\rangle)/2$. Note that the signature of the thermal average is the global factor $\tanh(\beta\Delta)$, reminiscence of the eigenvalues of the Hamiltonian given by Eq. (2). Moreover, the heat capacity at constant volume is expressed for a chiral system as

$$C_v = k_B \beta^2 \Delta^2 \text{sech}^2 \beta\Delta \quad (10)$$

displaying the so-called Schottky anomaly occurring in systems with a limited number of energy levels. This thermodynamic expression for the heat capacity is usually derived from one of the two following expressions

$$C_v = \frac{\partial U}{\partial T} = k_B \beta^2 \frac{\partial^2 Z}{\partial \beta^2} \quad (11)$$

where U is the internal energy. Alternatively, the heat capacity can also be obtained from the entropy as

$$C_v = T \frac{\partial S}{\partial T} \quad (12)$$

with

$$S = k_B \ln[2e^{-\beta E_0} \cosh(\beta\Delta)]. \quad (13)$$

A critical temperature given by

$$T_c \sim \frac{\Delta}{1.2k_B} \quad (14)$$

is derived when $\langle z \rangle_\beta$ displays an inflection point and the heat capacity a maximum as a function of the temperature. At temperatures higher than T_c , the role of ϵ is masked by thermal effects which tend to wash out the population difference z (racemization). At temperatures lower than T_c , the value of the ratio ϵ/δ is determinant. When this ratio is close to unity, $\langle z \rangle_\beta$ is determined by the competition between the tunneling and the asymmetry or bias. When it is much greater than one, the tunneling process plays a minor role and $\langle z \rangle_\beta$ keeps more or less its initial value. Finally, when this ratio is much less than one, the racemization is always present. At very low temperatures, cold or ultracold regimes, a chiral

two level bosonic system could display condensation as well as a discontinuity in the heat capacity (reduced temperatures $k_B T/\Delta \leq 1$) [30].

These populations and coherences have been evaluated from the stochastic dynamics leading to numerical values in agreement with Eqs. (8) [17]. Furthermore, depending on the temperature, the incoherent and coherent tunneling regimes were fitted to path-integral analytical expressions beyond the so-called noninteracting blip approximation in order to extract information of the frequencies and damping factors of the non-isolated system in its time evolution to thermodynamic equilibrium. As mentioned previously, the critical temperature issued from the maximum of the heat capacity [29] is considered the threshold temperature where quantum effects become dominant; in other words, where the coherent regime is well established. Furthermore, the thermal average of the energy (9) can also be easily extracted from the time evolution of the chiral system from the effective Hamiltonian function defined by Eq. (7) at asymptotic times, that is,

$$\langle E \rangle_\beta = \langle H_{\gamma,\xi}(z, \Phi) \rangle_\beta. \quad (15)$$

On the other hand, when phase difference thermal values or, equivalently, the so-called coherence factor, $\langle \cos \Phi \rangle_\beta$, has to be evaluated, a different strategy should be followed. Note that the coherence factor is directly related to one of our two canonical variables. One could think that thermal averages could also be extracted analytically from its own definition in standard statistical mechanics, that is,

$$\langle F(z, \Phi) \rangle_\beta = \frac{1}{Z_c} \int_{-1}^1 dz \int_0^{2\pi} d\Phi F(z, \Phi) e^{-\beta H_0(z, \Phi)} \quad (16)$$

where $F(z, \Phi)$ is a general function of the canonical variables z and Φ and H_0 is given by Eq. (2). However, a straightforward analytical integration of the corresponding partition function Z_c gives

$$Z_c = \frac{4\pi}{\beta\Delta} \sinh\beta\Delta \quad (17)$$

which is quite different from the quantum partition function mentioned above ($Z = 2 \cosh(\beta\Delta)$). The origin of this discrepancy is clearly due to the fact that the effective Hamiltonian H_0 and the phenomenological quantum Hamiltonian H can not be replaced each other. Thus, we have added a subindex c (from classical) to the partition function issued from H_0 . Following Eq. (16), the corresponding thermal averages of z , E , σ_x , etc. can also be easily evaluated analytically. In principle, one should expect agreement when the

dynamical conditions are approaching those of a classical system (for example, by increasing the temperature). Special attention deserves the thermal average of Φ and $\cos \Phi$ [31]. In particular, the quantum thermal average of the coherence factor (which provides the degree of coherence of the chiral system) is given by

$$\langle \cos \Phi \rangle_\beta = \frac{\sum_n \langle n | \cos \Phi | n \rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \quad (18)$$

where the sum over n runs only two values, the two eigenstates. The quantum averages of $\cos \Phi$ over these two eigenstates could be carried out following Ref. [32]. An alternative and simpler procedure can also be followed. Due to the fact the equilibrium values of $\langle z \rangle_\beta$ and $\langle \sigma_x \rangle_\beta$, Eq. (8), are well reproduced from our stochastic calculations, the values of $\langle \cos \Phi \rangle_\beta$ could be extracted from those thermal averages. Thus, we have that

$$\langle \cos \Phi \rangle_\beta = \frac{(\delta/\Delta) \tanh(\beta\Delta)}{\sqrt{1 - (\epsilon/\Delta)^2 \tanh^2(\beta\Delta)}}. \quad (19)$$

On the other hand, for open systems, the coupling to the heat bath defining the temperature is in general finite and weak. The definition of the internal energy is not obvious. Usually, one is inclined to assume that

$$U = \frac{\partial \langle E \rangle_\beta}{\partial T} \quad (20)$$

where this energy is seen as the average energy of the chiral system in the presence of the thermal bath and its mutual interaction. In our context, it is the non-conserved energy given by Eqs. (7) and (15). If we want to follow the second expression, the partition function of the reduced system has to be used. As pointed out previously [19, 33, 34], these two routes may differ yielding different results. In particular, the second route leads to negative values at very low temperatures when dealing with free damped particles. Specific heat anomalies in open quantum systems are nowadays an important topic. It can be used a different strategy. The heat capacity can also be evaluated from the energy fluctuations of the chiral system as

$$C_v = \frac{1}{k_B T^2} \langle (E - \langle E \rangle_\beta)^2 \rangle_\beta \quad (21)$$

Following this route, the heat capacity is time-dependent reaching a constant value at asymptotic times. Very good agreement has been reported [18] when comparing with the standard thermodynamics values.

C. Quantum stochastic resonance for an open chiral two level system

Although we have assumed so far that both δ and ϵ are time-independent variables, a much more rich dynamics is obtained when considering one of them (or both) as being certain functions of time. In order to simplify the discussion presented here, only a time varying bias is going to be considered. As previously mentioned, time-dependent bias effects have been proposed to enhance the very elusive parity violation effects in molecules [22–24]. When the driving field enters the dynamics by making the replacement

$$\epsilon \rightarrow \tilde{\epsilon}(t) = \epsilon + \epsilon_1 \cos(\omega t), \quad (22)$$

where ω is the driving frequency and ϵ_1 is the amplitude of the driving field, the Hamiltonian function for the isolated TLS is modified according to

$$\tilde{H}_0 = -\sqrt{1-z^2} \cos \Phi + \frac{\tilde{\epsilon}}{\delta} z, \quad (23)$$

where the time dependence is now also in the bias term, modulating then the competing mechanism between the tunneling and the asymmetry of the TLS. Again, within the Markovian regime, the corresponding stochastic dynamics is given by the following coupled differential equations

$$\begin{aligned} \dot{z} &= -\sqrt{1-z^2} \sin \Phi - \gamma \dot{\Phi}(t) + \xi(t) \\ \dot{\Phi} &= \frac{z}{\sqrt{1-z^2}} \cos \Phi + \frac{\tilde{\epsilon}}{\delta}. \end{aligned} \quad (24)$$

In the deep tunneling regime, the TLS approximation is particularly useful and the quantity of interest is the so-called power spectrum [1]

$$S(\nu) = \int_{-\infty}^{\infty} \bar{C}^{asy}(\tau) e^{i\nu\tau} d\tau \quad (25)$$

where $\bar{C}^{asy}(\tau)$ is the time-averaged steady-state (asymptotic) population autocorrelation function

$$\bar{C}^{asy}(\tau) \equiv \lim_{\tau \rightarrow \infty} \frac{\omega}{2\pi} \text{Re} \int_0^{2\pi/\omega} \langle z(t+\tau)z(t) \rangle dt, \quad (26)$$

which can be expressed as

$$\bar{C}^{asy}(\tau) = \sum_{m=-\infty}^{\infty} |P_m(\omega, \epsilon_1)|^2 e^{-im\omega\tau} \quad (27)$$

P_m being the Fourier coefficients of the asymptotic population

$$\lim_{t \rightarrow \infty} z(t) = z^{asy}(t) = \sum_{m=-\infty}^{\infty} P_m(\omega, \epsilon_1) e^{-im\omega t}. \quad (28)$$

Taking into account equations (25) and (27), the power spectrum is expressed as

$$\begin{aligned} S(\nu) &= 2\pi \sum_{m=-\infty}^{\infty} |P_m(\omega, \epsilon_1)|^2 \delta(\nu - m\omega) \\ &= \frac{(\hbar\epsilon_1)^2}{2} \sum_{m=-\infty}^{\infty} \eta_m(\omega, \epsilon_1) \delta(\nu - m\omega). \end{aligned} \quad (29)$$

where η_m are known as the power amplitudes

$$\eta_m(\omega, \epsilon_1) = 4\pi |P_m(\omega, \epsilon_1)|^2 / \hbar\epsilon_1, \quad (30)$$

which correspond to the different harmonics of the driving frequency. This is the way to observe the QSR. Classically, the stochastic resonance is maximal for the symmetric system ($\epsilon = 0$) whereas, in the deep quantum regime, the QSR is only effective for the asymmetric system or static bias [1]. Moreover, at low temperatures (coherent regime), the QSR occurs when the frequency of the driving force is near to fractional values of the static bias ($\omega = \epsilon/n$, $n = 1, 2, 3, \dots$). At these values, the amplitude of the fundamental frequency in the power spectrum is reinforced and the coherent motion induced by the driving force is amplified [1]. Even more, when the amplitude of the driving force is smaller than the static bias, the power spectrum shows an amplification as a function of the temperature.

Furthermore, other magnitudes derived from the asymptotic behavior of the population also display the same behavior with time as, for instance, the internal energy U^{asy} and the specific heat C_v^{asy}

$$U^{asy}(t) = \sum_{m=-\infty}^{\infty} U_m(\omega, \epsilon_1) e^{-im\omega t}, \quad (31)$$

$$C_v^{asy}(t) = \sum_{m=-\infty}^{\infty} C_{v,m}(\omega, \epsilon_1) e^{-im\omega t}, \quad (32)$$

where $C_{v,m} = \partial U_m / \partial T$. In general, we have that

$$U_m(\omega, \epsilon_1) = -\frac{\Delta^2}{\epsilon} P_m(\omega, \epsilon_1) \quad (33)$$

and

$$C_{v,m}(\omega, \epsilon_1) = -\frac{\Delta^2}{\epsilon} \frac{\partial P_m(\omega, \epsilon_1)}{\partial T}. \quad (34)$$

In the linear response regime, which is the appropriate regime to study the tiny P-odd effect predicted, only the first two contributions, $m = 0$ and $m = \pm 1$ of $z^{asy}(t)$ are important. Following the standard procedure [1], the zeroth-order (in the absence of driving) contribution gives the population difference in thermal equilibrium without external driving field, Equation (8). The non-zero optical activity derived from this result is due to the PVED between enantiomers, ϵ . The second contribution given by P_1 is related by Kubo's formula to the linear susceptibility of the system, $\hat{\chi}$. Following the standard procedure [1], assuming small friction and the restrictions $\omega\beta \ll 1$, $\epsilon_1\beta \ll 1$ and $\epsilon_1 < \epsilon$, this contribution of the response of our system to the external amplitude ϵ_1 is expressed as [26]

$$P_1(\omega, \epsilon_1) = \epsilon_1 \hat{\chi}(\omega) = \frac{\epsilon_1}{4} \frac{\lambda^2}{\lambda^2 + \omega^2} f(\beta, \epsilon), \quad (35)$$

where

$$f(\beta, \epsilon) = \beta \text{sech}^2 \beta \epsilon \quad (36)$$

where $\lambda = \pi\Delta^2/(2\omega_c)$, ω_c being a cutoff frequency. As a function of the temperature, P_1 displays a maximum when

$$\beta \epsilon \tanh \beta \epsilon = 1 \quad (37)$$

leading to a critical temperature of

$$T_{qsr} \propto \frac{\epsilon}{k_B} \quad (38)$$

which means that due to the fact the ϵ parameter is extremely small, the maximum lies in the ultracold regime and is also independent on the tunneling rate.

III. RESULTS

Several comments are in order when solving numerically Eqs. (5) or (24). As previously used, units along this work are dimensionless. By doing this, we are considering a general dynamics where any chiral molecule can be represented. For example, if for a given chiral molecule $\delta = 10^{-4}$ meV, we set this value to be 1 after passing the tunneling rate to inverse of atomic units of time, $3.675 \cdot 10^{-5}$. In all the calculation, we have further assumed that $\delta \sim \epsilon$ in order to properly analyze the competition between tunneling and asymmetry or between

delocalization and localization. With the time step used, $\gamma = 0.1$ or 0.01 (dimensionless rate) is a good parameter for the Ohmic friction. When working on thermodynamic functions, reduced units have also been employed, that is, energies and temperatures are divided by Δ . As mentioned previously, at high temperatures, $\beta^{-1} \gg \gamma$, thermal effects are going to be predominant over quantum effects which become relevant, in general, at times of the order of or less than the so-called thermal time, β (in atomic units). However, at very low temperatures, $\beta^{-1} \ll \gamma$, the noise is usually colored and its auto-correlation function is complex, our approach being no longer valid. Here, a canonical (Maxwell–Boltzman) distribution is assumed and only classical noise is considered since the ultracold regime is not going to be analyzed. On the other hand, the role of initial conditions has been extensively discussed in the literature (see, for example, [1, 2]); for practical purposes, the chiral system will be prepared in one of its two states, left or right ($z(0) = 0.999$ or -0.999 in order to avoid initial singularities, and very far from the equilibrium condition), and the initial phase difference $\Phi(0)$ will be uniformly distributed around the interval $[-\pi, \pi]$. The stochastic trajectories issued then from solving Eq. (5) are dependent on the five dimensional parameter space $(\epsilon, \epsilon_1, \delta, \gamma, T)$. When running trajectories, there are some of them visiting "nonphysical" regions, that is, $|z| > 1$. This drawback is mainly associated with the intensity of the noise since, for large values of it (which depends on both the temperature and the friction coefficient), the stochastic z -trajectories can become unbounded. To overcome this problem, we have implemented a *reflecting* condition such that when the trajectory reaches $z > 1$, we change its value to $2 - z$ (or when $z < -1$, we pass to $-2 + z$). After our experience, the number of such pathological trajectories is very small and over a very large number of trajectories in order to have a good statistics, their weight is negligible. The general strategy consist of solving the pair of non-linear coupled equations (5) or (24) for the canonical variables under the action of a Gaussian white noise, which is implemented by using an Ermak-like approach [35, 36]. Note that in the Langevin-like coupled equations to be solved, the noise term only appears in the equation of motion of the z -variable. The time step used is 10^{-2} (dimensionless units) for all the cases analyzed. As noted in [15], unstable trajectories can also be found for certain values of ϵ , δ and γ in the simple case of dissipative but non-noisy dynamics. As this problem persists in case of dealing with stochastic trajectories, not every triplet $(\epsilon, \delta, \gamma)$ gives place to a stable trajectory. In these cases, the time evolution of each individual trajectory is not possible and a previous stability

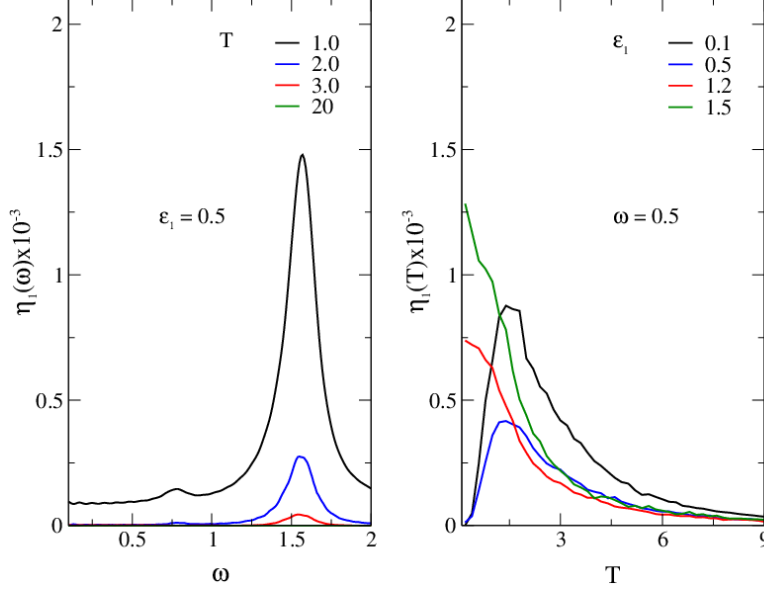


Figure 1: Power amplitude η_1 of the fundamental frequency in the power spectrum as a function of the frequency of the external driving force (left panel) and the temperature (right panel). The results are obtained for $\epsilon = 1.2$, $\delta = 1.0$ and $\gamma = 0.1$

analysis is mandatory. However, in the stable case, a satisfactory description of population differences and coherences, average energies and heat capacity have been achieved by running up to 10^4 trajectories as already mentioned [17, 18].

The time step used is finally $\gamma = 0.1$ (dimensionless rate) and a canonical (Maxwell-Boltzmann) distribution is assumed, only classical noise being considered.

The QSR can be observed from the power amplitudes. In Fig. 1, the power amplitude η_1 of the power spectrum as a function of the frequency of the external driving force (left panel) and the temperature (right panel). The results are obtained for $\epsilon = 1.2$, $\delta = 1.0$ and $\gamma = 0.1$. In the right panel, three different regimes are clearly displayed, for a given driving frequency, as a function of the temperature. In the case of $\epsilon_1 > \epsilon$, the power amplitude exhibits a more or less exponential decay as the temperature increases. When $\epsilon_1 < \epsilon$, a minimum in the power amplitude followed by a maximum (stochastic resonance) is observed at low temperatures, around the critical temperatures T_c and T_{qsr} . Finally, if $\epsilon_1 \ll \epsilon$, the resonance is observed and the evolution of the system could be described in the framework of the linear response theory [1]. Moreover, in the left panel of Fig. 1, η_1 is plotted as a function of ω for different temperatures. As other theories predict, a large peak near 1.5 ($\epsilon = 1.2$) and other small peak around 0.75 ($\omega = \epsilon/2$) are observed. We also

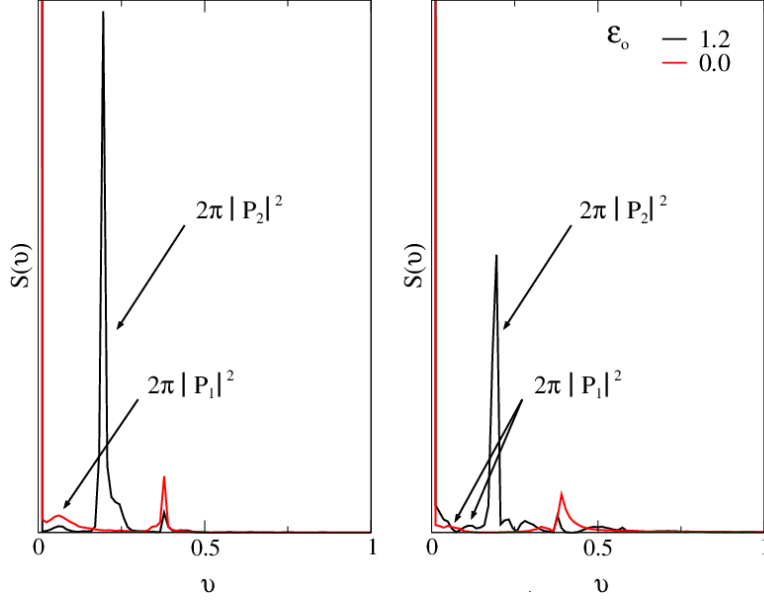


Figure 2: Suppression of the second term, P_1 , of the power spectrum for a symmetric (unbiased) potential. See text for details.

note that these peaks disappear as temperature increases. From Equation (35), a simple analytical expression can be easily deduced for this power amplitude.

A very interesting and distinguishing feature between biased and unbiased systems is shown clearly in Fig. 2. The second Fourier coefficient of the power spectrum is completely suppressed for a symmetric (unbiased) potential. In the left (right) panel, the dynamics is starting from (out of) the thermodynamical equilibrium. In both cases, the parameters are $\epsilon_1 = 0.5$, $\omega = 0.5$, $\gamma = 0.1$, $\delta = 1.0$. We note that, after removing spurious bias terms, this suppression could be used as a signal of parity violation in chiral molecules.

Interestingly enough, the features observed in the amplitude of the fundamental frequency of the power spectrum are also revealed in the behavior of other magnitudes such as the population difference. In Fig. 3, average population difference, $\langle z_0 \rangle$, as a function of the frequency of the external driving force (left panel) and as a function of the temperature (right panel) are displayed. The results are obtained for $\epsilon = 1.2$, $\delta = 1.0$ and $\gamma = 0.1$. It is clearly observed that the population difference exhibit well defined peaks around the fractional values of the static bias even for frequency values around $\omega = \epsilon/3$. When the temperature is increasing more and more, an incoherent regime is rapidly established. For the same case, in Figure (4), the power amplitude $\eta_1(\omega)$ of the fundamental frequency in the power spectrum are plotted when propagation is starting far from thermodynamical

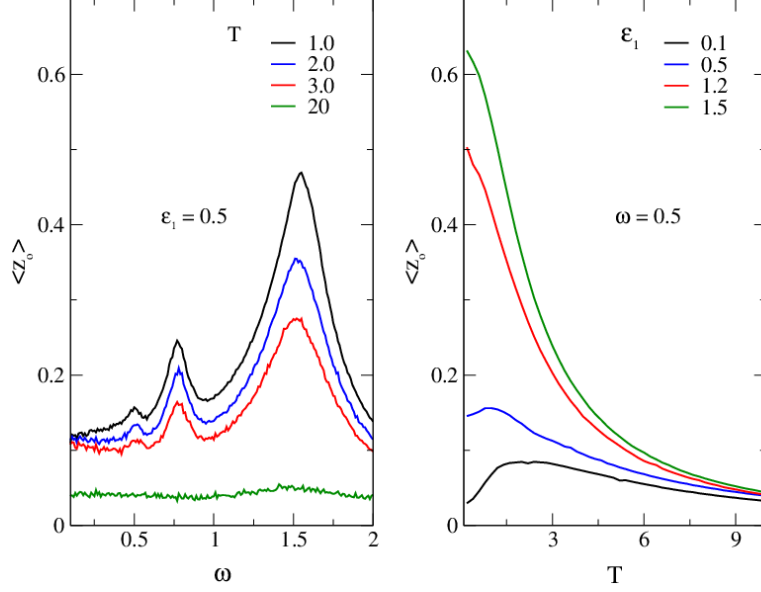


Figure 3: Average population difference, $\langle z_0 \rangle$, as a function of the frequency of the external driving force (left panel) and as a function of the temperature (right panel). The results are obtained for $\epsilon = 1.2$, $\delta = 1.0$ and $\gamma = 0.1$

equilibrium values (left panel) and close to them (right panel). When simulations start far from the thermodynamical equilibrium, the amplitude of the peaks observed in $\eta_1(\omega)$ has been shown to be larger than those obtained starting closer.

In Figure 5, the heat capacity as a function of the frequency of the external bias for different temperatures. In these calculations, $\epsilon = 1.2$, $\epsilon_1 = 0.5$, $\delta = 1.0$ and $\gamma = 0.1$. This thermodynamics function shows a strong dependence on frequency of the bias for different temperatures. It is important to note the appearance of extrema in the same regions where average population differences display a maximum (see Figure 3). The same behavior is observed when starting the dynamics from nonequilibrium initial conditions. Different plots of the Fourier components of the internal energy and heat capacity at asymptotic times can also be easily analyzed in the light of Equations (32), (33) and (34).

IV. FINAL DISCUSSION

In previous works, we have successfully applied a Langevin canonical formalism to the stochastic dynamics of a non-isolated chiral TLS when reproducing some quantum thermodynamic functions (such as, the partition function and heat capacity). In this paper, as a

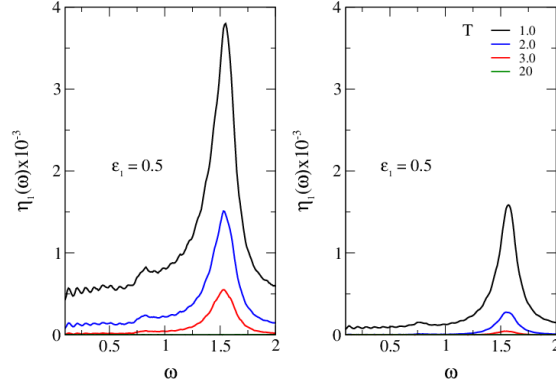


Figure 4: Power amplitude $\eta_1(\omega)$ of the fundamental frequency in the power spectrum when propagations started far from thermodynamical equilibrium values (left panel) and when they started close to the thermodynamical equilibrium values (right panel). The results are obtained for $\epsilon = 1.2$, $\epsilon_1 = 0.5$, $\delta = 1.0$ and $\gamma = 0.1$

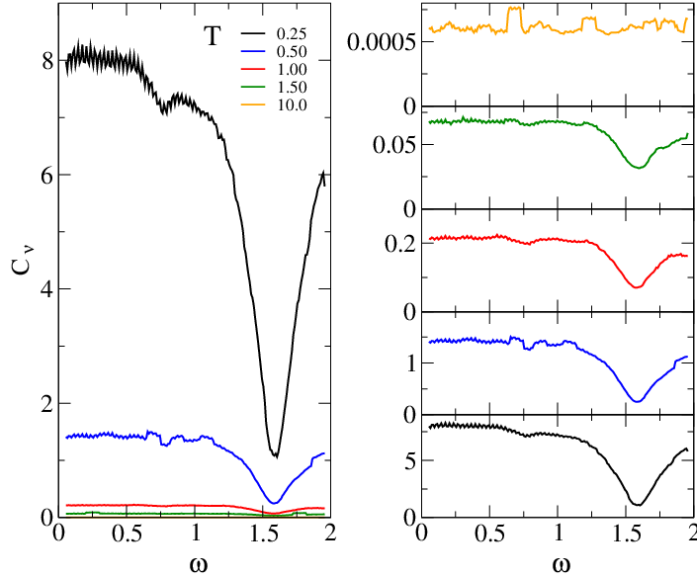


Figure 5: Heat capacity as a function of the frequency of the external bias for different temperatures. In the calculations $\epsilon = 1.2$, $\epsilon_1 = 0.5$, $\delta = 1.0$ and $\gamma = 0.1$

continuation and extension of our work, we have tackled the dynamics of the QSR. This resonance is considered as a well known cooperative effect of friction, noise and periodic driving occurring in a bistable system. Under the presence of the driving field, the heat capacity has also been analyzed at asymptotic times. We have assumed so far that the tunneling rate is a

constant value. Obviously, this rate could be considered to also be a function of time. This should have important implications in the detection of QSR in chiral molecular systems. Due to the fact that this stochastic dynamics is occurring at ultracold regimes, a sort of Bose-Einstein condensation could take place. Moreover, at this regime, the noise is usually colored with a complex time autocorrelation function. All of these ingredients should be incorporated to such a dynamics in order to improve the description of nonisolated chiral TLS. Work in this direction is now in progress.

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